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Synthesis and Stereochemistry of the Spin Adducts of a New Chiral Spin Trap, 3,5-Diphenyl-5-methylpyrroline-1-oxide

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ABSTRACT: The synthesized spin trap 3,5-diphenyl-5-methylpyrroline-1-oxide (**3**), its derivatives and spin adducts were studied using NMR, ESR and ENDOR spectroscopic methods. The structure of **3** was determined using x-ray analysis. The nitrone **3** was found to have a rigid structure. Two species were observed in the EPR and ENDOR spectra of the spin adducts of **3**, but not in the NMR spectra of its diamagnetic derivatives. These two species were attributed to those formed when the addends attack carbon-2 from both the *re* and *si* sides, resulting in *trans* (I) and *cis* (II) adducts in relation to the phenyl substituent in position 3. Therefore, these two species differ only through the substitution on carbon-2, whereby there are different steric interactions of the substituents within both species. The lack of observation of these two species in NMR spectra could be interpreted in terms of unfavourable relaxation times on the NMR time-scale. These species are observed in EPR and ENDOR spectra mainly because of their different β-C—H dihedral angles, which do not play a role in NMR spectroscopy. Both species have the ability to trap stereoselectively carbon- and oxygen-centred radicals, which occupy pseudo-equatorial and pseudo-axial positions, respectively. The occupation of oxygen-centred addends in the pseudo-axial positions is stabilized by the 'anomeric effects.' This nitrone **3** was found to have the ability to scavenge short-lived free radicals in both aqueous and non-aqueous solutions. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: EPR; ENDOR; spin trap; anomeric effect

INTRODUCTION

The electron spin resonance (ESR) technique of spin trapping has been widely used for the investigation of paramagnetic species in chemical, physical and biological systems.[1–4] The trap used should efficiently scavenge free radicals and afford persistent spin adducts.[5] The ability of ESR to detect low concentrations of free radicals and its sensitivity to their environment and molecular motions have contributed greatly to its popularity. The generally accepted view that free radicals are mediators of cellular responses such as cancer, ageing, oxidative stress[6,7] and ischaemia/reperfusion injury has greatly increased research activity in the field of spin trapping in biological systems.

Cyclic nitrones have shown more sensitivity to the structure of the radical addend.[8–13] It is interesting to consider the origin of the variation in the proton hyperfine splitting ($a_{\beta H}$) observed as a function of structure of the addend. The magnitude of this interaction is governed by the McConnell–Heller equation ($a_{\beta H} = B\rho_N \cos^2 \theta$), where B and ρ_N are constants and θ is the hyperconjugation angle. Thus, each group R added to the spin trap will have different steric and stereoelectronic characteristics and will therefore give rise to a different value for θ.

Several forms of chiral cyclic nitrones have been synthesized and used for the study of spin trapping stereochemistry by various investigators.[14–18] We earlier reported[18] the use of 5,5-dimethyl-3-phenylpyrroline-1-oxide in the stereoselective spin trapping of both carbon- and oxygen-centred radicals. In this paper, we report the synthesis and a spin trapping study of 3,5-diphenyl-5-methylpyrroline-1-oxide (**3**) and describe the EPR spectra obtained from a variety of spin adducts produced from trapping free radicals in both aqueous and non-aqueous solutions. This nitrone was synthesized as illustrated in Scheme 1.

EXPERIMENTAL

Syntheses

The nitrone **3** was prepared in a two-step synthetic route as shown in Scheme 1. Compound **1** was synthesized as reported earlier.[18] Addition of phenylmagnesium bromide to **1** led to the hydroxylamine **2**, whose subsequent oxidation with active lead oxide gave the spin trap **3**.

3,5-Diphenyl-5-methyl-*N*-hydroxypyrrolidine (2). A diethyl ether solution of **1** (6.72 g, 38.3 mmol) was added dropwise to phenylmagnesium

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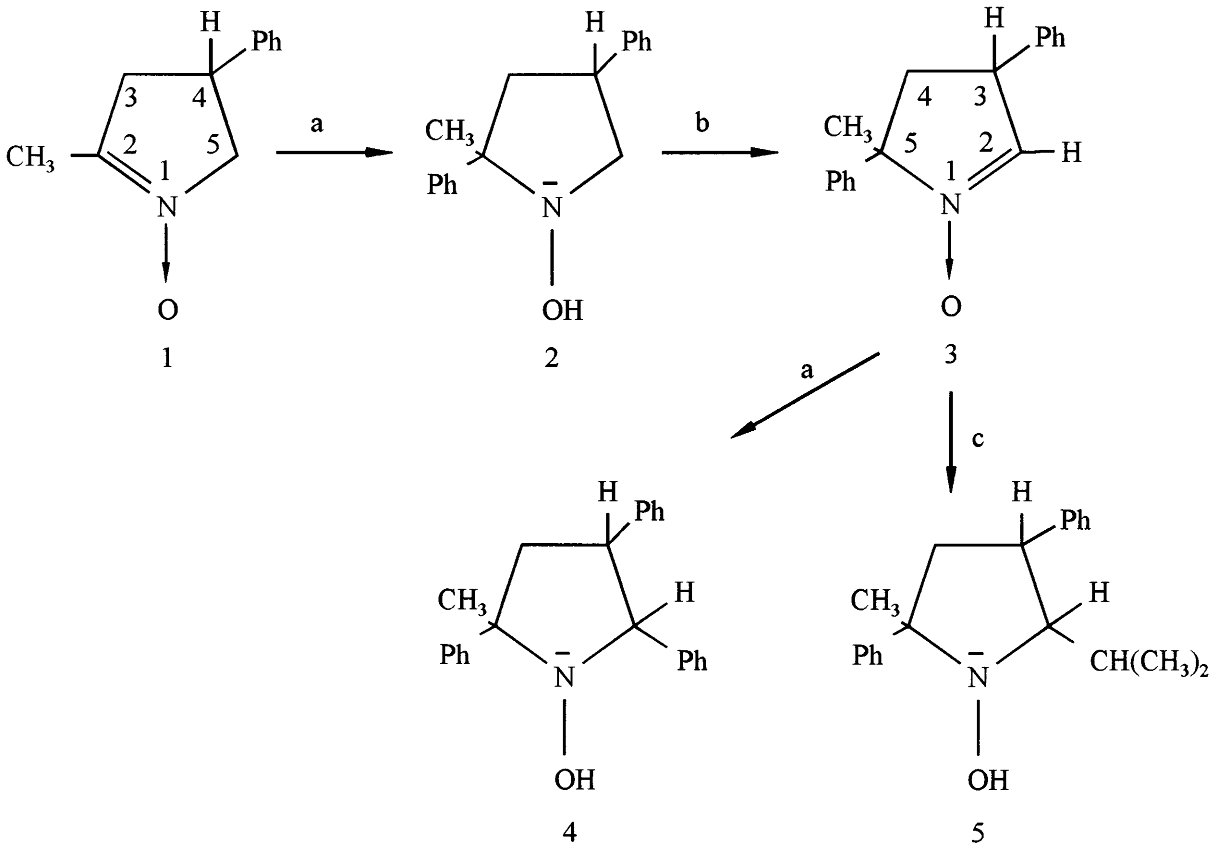

Scheme 1. Reagents: (a) PhMgBr; (b) active PbO_2 in benzene; (c) $CH_3CH(MgBr)CH_3$.

bromide (Aldrich) (77.2 mmol) at 0 °C under nitrogen. After refluxing and stirring for 2 h, the reaction mixture was cooled and 20 ml of saturated ammonium chloride solution were added. The aqueous phase was extracted three times with 50 ml portions of diethyl ether. The combined extracts were dried over $MgSO_4$ and rotary evaporated. The solid residue was recrystallized from hexane to give colourless crystals with a melting range of 150–152 °C and a yield of 7.13 g (73%).

IR (cm^{-1}): 1366 (N—O), 1484 (C—N), 3200 (O—H). ^{13}C NMR ($CDCl_3$): δ (ppm) 25.2 (CH_3), 41.7 (CH_2), 44.8 (PhCH) 63.8 (CH_2N), 72.8 ($PhCCH_3$), 105–146 (Ar—C). Mass spectrometry (MS): m/z 253.8 (M^+, 21%), 238.2 ($M^+ - 15$, 100), 222.3 ($M^+ - 31$, 26), 208.4 ($M^+ - 45$, 51), 193.2 ($M^+ - 60$, 64), 176.2 ($M^+ - 77$, 24), 91.2 ($C_7H_7^+$, 86), 77.2 ($C_6H_5^+$, 34). Elemental analysis: $C_{17}H_{19}NO$ (253.2): calculated C 80.59, H 7.56, N 5.53; found C 80.65, H 7.56, N 5.53%.

3,5-Diphenyl-5-methylpyrroline-1-oxide (3). To a solution of **2** (1 g, 3.95 mmol) in dry, warm benzene was added portionwise about 5 g of active PbO_2 under a nitrogen atmosphere and the mixture was stirred for 5 h at room temperature. After filtration of the reaction mixture and removal of the solvent under vacuum, the solid residue was recrystallized from hexane, giving 1.2 g (95%) of white crystals of **3** with m.p 88–90 °C.

IR (cm^{-1}): 1224 (N—O), 1558 (C=N). ^{13}C NMR ($CDCl_3$): δ (ppm) 26.3 (CH_3), 43.3 (CH_2), 48.1 (PhCH), 80.4 ($PhCCH_3$), 136.5 (C=N), 125–141 (Ar—C). MS: m/z 251.2 (M^+, 36%), 234.1 ($M^+ - 17$, 14), 221.2 ($M^+ - 30$, 24), 132.3 ($M^+ - 119$, 81), 104.2 ($CH_3C_6H_5^+$, 100), 91.2 ($C_7H_7^+$, 24), 77.2 ($C_6H_5^+$, 50). Elemental analysis: $C_{17}H_{19}NO$ (251.2): calculated C 81.23, H 6.82, N 5.58; found C 81.29, H 6.77, N 5.57%.

Spin adduct/radical addend generation

Spin adduct preparation was typically performed in toluene or aqueous solutions at room temperature. Hydroxyalkyl radicals were generated by the method of hydrogen abstraction by the triplet state of photoexcited benzophenone.[19,20]

The hydroxyl spin adducts were generated by irradiating a solution of 2% H_2O_2 in water containing the spin trap with UV radiation from a low-pressure mercury lamp.[16,21] Similar irradiation was used for the generation of *tert*-butoxy radicals from a solution of the spin trap and di-*tert*-butyl peroxide in benzene. The adducts of the anions were prepared by the addition of Grignard compounds (purchased from Aldrich) followed by oxidation with air or lead dioxide. The hydrogen atom spin adducts were also generated by the oxidation of their corresponding hydroxylamines. Oxygen was removed from experimental solutions by bubbling with argon for 5 min.

Instrumentation

EPR and ENDOR spectra were acquired on Bruker ESP 3OO E and ER 810 spectrometers, respectively. NMR spectra were obtained on Bruker AC 250 (62.9, 250 MHz) and WM 400 (400 MHz) spectrometers. Mass spectra were recorded using a TSQ 70 (Finnigan MAT) and MAT 711A (Finnigan) and infrared spectra on a Perkin-Elmer series Fourier transform IR spectrometer.

X-ray diffraction

The intensities for the structure determination were collected on a automated-single-crystal CAD4 diffractome-

Table 1. X-ray data collection and structure refinement parameters

Crystal dimensions (mm)	0.3 × 0.25 × 0.25
Empirical formula	$C_{17}H_{17}NO$
M	251.32
Space group	$R\bar{3}$
Unit cell dimensions	$a = 29.485$ (1)Å
	$b = 29.485$ (1)Å
	$c = 8.179$ (1)Å
	$\alpha = 90°$
	$\beta = 90°$
	$\gamma = 120°$
V(Å^3)	6157.8 (8)
Z	18
D_c(g cm^{-3})	1.220
Radiation used (λ)	Cu Kα (1.541 84)
Data collection method	ω scans
Linear absorption coefficient (mm^{-1})	0.724
Weighting scheme	$1/[\sigma^2(F_o)^2 + 0.0516P^2 + 4.2734P)]$ with $P = (F_o{}^2 + 2F_c{}^2)/3$
Reflections collected	4303
θ Range	5.19–64.86
Index ranges	h, −34 to 34; k, −27 to 19; l, −9 to 9
Independent reflections/R_{int}	2190/0.0303
Reflections observed [$I > 2\sigma(I)$]	1852
Parameters	241
R_1(obs)/R_1 (all)	0.0403/0.0483
$wR2$(obs)/$wR2$(all)	0.1033/0.1101
Goof (F^2)	1.059

Table 2. Selected bond lengths (Å) and angles (°) in **3**

N1—O1	1.290 (1)	N1—C2	1.298 (2)
C2—C3	1.488 (2)	C3—C4	1.538 (2)
C3—C21	1.509 (2)	C4—C5	1.533 (2)
C5—C6	1.520 (2)	C5—C11	1.525 (2)
C5—N1	1.510 (2)		
C2—N1—O1	128.6 (1)	C5—N1—O1	119.6 (1)
N1—C2—C3	112.7 (1)	C2—C3—C4	101.4 (1)
C2—C3—C21	113.4 (1)	C4—C3—C21	115.6 (1)
C4—C5—N1	100.4 (1)	C4—C5—C6	114.1 (1)
C4—C5—C11	111.8 (1)	C6—C5—C11	112.4 (2)

ter (Enraf Nonius). The unit cell dimensions were determined from 25 high-angle reflections. The structure was solved by the Patterson method using SHELXS86.[22] Refinement was performed with SHELXL93.[23] The positions of all atoms (including hydrogen) were derived from subsequent Fourier maps. All non-hydrogen atoms were refined with anisotropic thermal parameters. More details on data collection and processing are contained in Table 1. Selected bond lengths and angles are summarized in Table 2. Supplementary material of the crystal structure determination

Table 3. ^{1}H NMR data for compounds **2–5** in $CDCl_3$ at room temperature

Compound	CH_3	PhCH	—NCH—	CH_2C	CH=N	CH_2N
2	1.63	3.4		2.27, 2.81		3.3, 3.57
	s	m		2dd; 8.8		2dd; 7.0
				9.0, 13.1 Hz		8.1, 11.0 Hz
3	1.91	4.01		2.27, 3.01	7.17	
	s	m; 2.4,		2dd; 7.9	d; 2.4 Hz	
		7.9, 9.8 Hz		9.3, 12.8 Hz		
4	1.71	3.13	4.25	2.24, 2.49		
	s	m; 8.73	d	2dd; 8.68,		
		10.27 Hz	10.30 Hz	10.30, 13.44 Hz		
5[a]	1.65	3.05	3.40	2.01, 2.43		
	s	m; 8.60,	2d; 3.60,	2dd; 8.46,		
		9.82 Hz	9.97 Hz	10.03, 13.25 Hz		

[a] Additional absorptions observed for the addend are CH_3 0.77, 1.01; 2d, 6.95, 7.04 Hz.

has been deposited with the Fachinformationszentrum Karlsruhe (Eggenstein–Leopoldshafen Germany), and can be ordered under the number CSD-XXXXXX.

RESULTS

Structural and conformational analyses of compounds **2**–**5** were performed using NMR spectroscopy and x-ray analysis. The ^{1}H NMR spectra, whose data are given in Table 3, show one intense single signal upfield which can be attributed to the methyl group in position 5 in all cases. The methylene protons in position 3 or 4 are diastereotopic, and consequently spin–spin coupling with one another and with a methyne proton in position 4 or 3 is observed. Therefore, the signal of these nuclei is a complex multiplet. The CH_2 group adjacent to the nitrogen in **2** shows a very similar structure, self-evidently. The interpretation of the other signals was straightforward.

X-ray analysis of nitrone **3** shows that it crystallizes in a centrosymmetric crystal system $R\bar{3}$ with an inversion centre, which consists of a pair of enantiomeric diastereomers with the configurations *RS′* and *SR′*. This analysis showed that the phenyl groups on carbons-3 and -5 assume pseudo-equatorial and pseudo-axial positions, respectively (Fig. 1). This nitrone crystallizes in the *trans* form, whereby the two phenyl substituents are found on opposite sides of the five-membered ring.

The EPR spectra of all the spin adducts of **3** show the existence of two species, as shown in Table 2. This is clearly illustrated by the EPR spectrum of the *tert*-butoxy adduct [Fig. 2(A)]. A computer simulation is shown in Fig. 2(B), assuming that the two species have the same g value. The proton ENDOR spectra for this spin adduct **16** (see Fig. 3) confirms the existence of two species. The signals of the β-protons for species I would appear at 9.4 and 38.0 MHz, whereas for nitroxide II ENDOR frequencies ν_E at 3.8 and 24.8 MHz are expected. For technical reasons, signals below 5 and above 30 MHz are hardly detected. Therefore, the signals observed experimentally are found at 9.4 and 24.8 MHz. An extra smaller coupling of 0.04 mT is observed in the ENDOR spectrum of the second species.

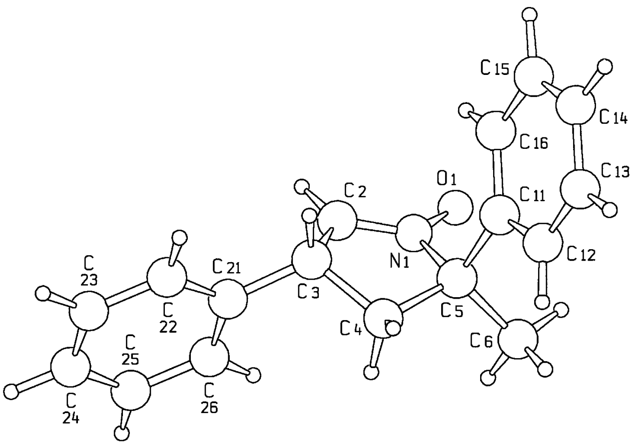

Figure 1. Crystal structure representation[24] of **3**.

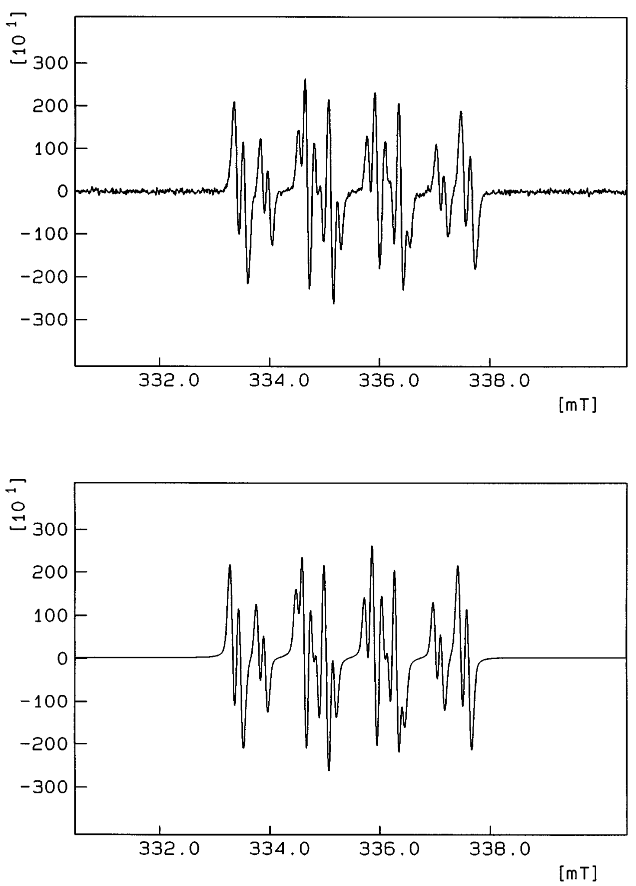

Figure 2. (A) EPR spectrum of the spin adduct **16** of nitrone **3** with *tert*-butoxy radicals in toluene; (B) simulated. The arrows a and b show the EPR field settings for measurement of ENDOR signals for species I and II, respectively.

Carbon-centred spin adducts of species I and II have β-hydrogen coupling constants in the ranges 2.1–2.4 and 1.6–2.05 mT, respectively. Notable exceptions are those of CH_3 (1.430 mT) and $CH_2{=}CH$ (1.364 mT) for species II. Spin adducts of oxygen-centred radicals have relatively low $a_{\beta\text{-H}}$ values for both species. There was no wide variation in the nitrogen splitting constants (1.4 ± 0.1 mT) of all the spin adducts studied, except for the second species of the *tert*-butoxy radical (1.25 mT). A γ-hydrogen splitting constant was observed only for species I of the phenyl adduct **12**.

The nitroxides **6**–**15** derived from carbon-centred adducts show βH-C—M dihedral angles (θ) for species I and II in the ranges 19–26.5 and 29.0–44.5°, respectively. The oxygen-centred spin adducts showed relatively high values of θ for both species of $>40°$. The method of determination of the constant $B\rho_N$ (2.66 mT) will be discussed later. Two species were not observed for the H-adduct.

Finally, it should be mentioned that a nitrogen ENDOR experiment was only successful with species II of the spin adduct **7** (Fig. 4). The intense pairs of lines centred at 14.3 MHz are due to unassigned γ-protons.

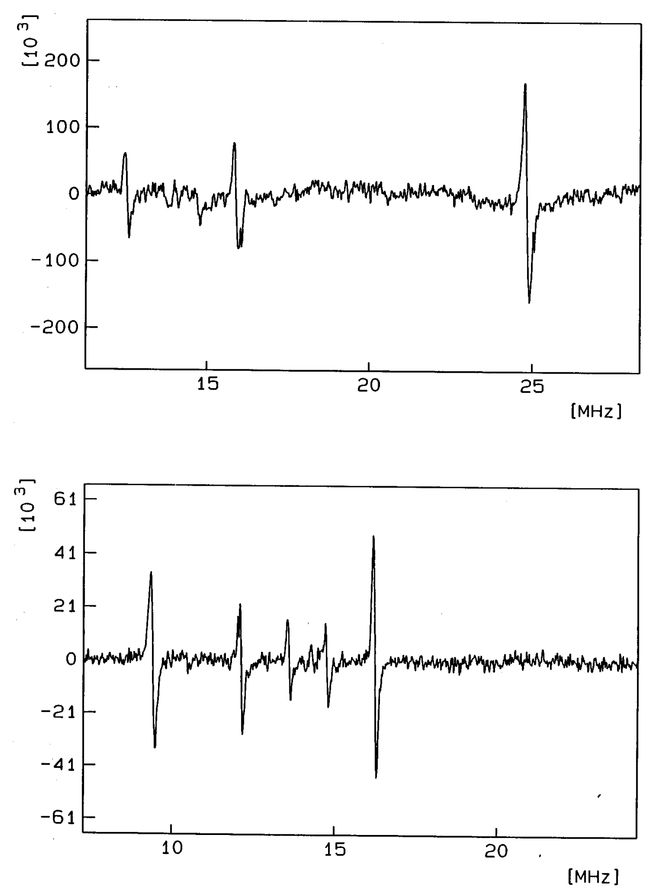

Figure 3. ENDOR spectra for the two species of the *tert*-butoxy spin adduct **16** in toluene at 213 K, $\nu_{LH} = 14.3$ MHz. (a) Species I ($\nu_E = 9.4$ MHz, 1.693 mT); (b) species II ($\nu_E = 24.8$ MHz, 0.75 mT).

The signal at 11.6 MHz corresponds to the low-frequency enhancement due to the coupling of the β-proton. The high-frequency line could not be observed for technical reasons.

DISCUSSION

The methyl group and methyne proton in position 3 of nitrone **3** absorb downfield compared with the corresponding ones in **2**, **4** and **5**. This can be attributed to the presence of a double bond in the pyrroline ring of the former. The methylene protons in **2**–**5** show a doublet of doublets because of their diastereotopic nature. This indicates the structural rigidity of these compounds in solution. The observed large coupling constant of *ca.* 13 Hz has to be attributed to the geminal coupling between these protons.

The existence of two radical species was confirmed by the EPR and ENDOR investigations of the spin adducts of nitrone **3**. EPR temperature variations studies showed no significant change in the β-H splitting constants except for the linewidth broadening with decreasing temperature resulting from anisotropic contributions,[25] indicating that the two species are not conformers but diastereomeric species. Diastereomers have been known to have different chemical and spectral properties.[26–28] As shown in Fig. 1, the phenyl substituents on carbons-3 and -5 have assumed such a conformation that allows easy attack by the addend on the sp^2-carbon in position 2 from both the *re* and *si* sides of the molecule, leading to the species I and II, respectively. These species can be clearly understood when looked at as *trans* (I) and *cis* (II) in relation to the phenyl substituent in position 3. These two species were not observed in the NMR spectra. This could be attributed to a conformational interconversion fast on the NMR time-scale. The observation of these two species in the EPR spectra is a result of the different β-H coupling constants which depend on the β-C—H dihedral angles. These angles do not play a significant role in NMR spectroscopy.

Steric interactions in species II between the phenyl group in position 3 and the addend causes an increase

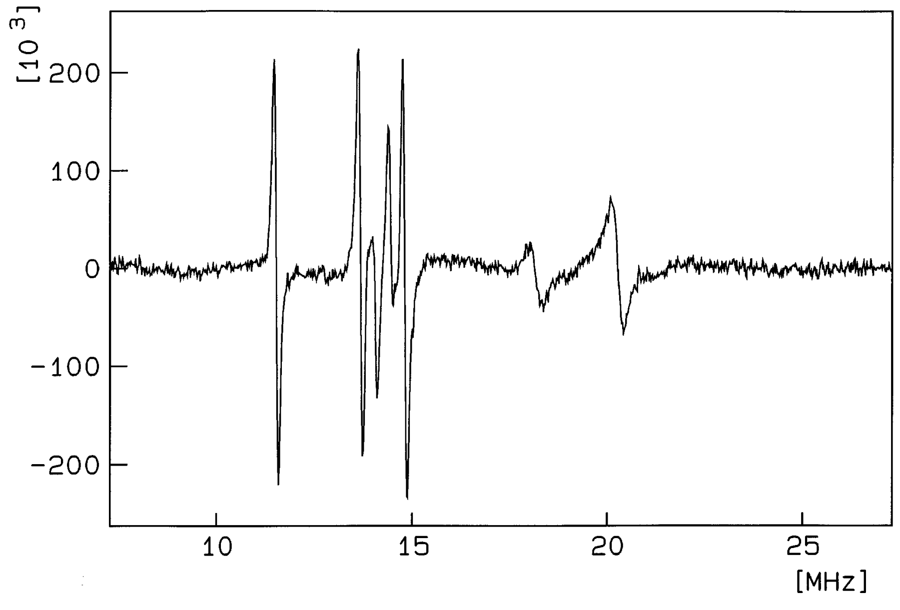

Figure 4. ENDOR spectrum for the second species of nitroxide **7** at 273 K in toluene, $\nu_{LH} = 14.3$ MHz, $\nu_{LN} = 1$ MHz.

in the β-C—H dihedral angles, resulting in lower $a_{\beta H}$ values. Such interactions play a minor role for species I. In general, the two species only differ through the substitution on carbon-2. The dihedral angles of various spin adducts of **3** were calculated using a $B\rho_N$ constant of 2.66 mT, which was determined from the β-hydrogen splitting constants of the H-adduct **18** using the McConnell–Heller equation. This value can be assumed to be applicable to all spin adducts of **3** because of the structural rigidity of the conformations. This structural rigidity of these five-membered ring adducts is well illustrated by the hydroxylamine **4**, whose two methyne protons have a coupling constant of 10.30 Hz, indicating that they occupy pseudo-axial positions, according to the Karplus equation. This interpretation of structural rigidity can also be applied to the nitroxides whereby the homolytic breakage of the O—H bond or lack of it in the structure causes no significant change in the conformations of the five-membered rings.

Owing to the small differences in the nitrogen splitting constants and the similarity of the g values significant differences in the spin density distribution in the pyrroline ring and its substituents are not expected. Diastereotopic protons reported in the literature[29] show only small differences in their splittings. Therefore, the observed large differences in the $a_{\beta H}$ values of the two species can only be interpreted in terms of relatively large differences in the dihedral angles, as shown in Table 4.

It can be concluded from the large differences in the dihedral angles of these diastereomers that there are strong interactions between the substituents at the chiral centres. The nitroxides **6**–**15** with aliphatic addends have β-C—H dihedral angles $<45°$. Such angles indicate that the β-hydrogens occupy the pseudo-axial positions in both species. Owing to the stabilization of the 'anomeric effects,'[18,30,31] the oxygen-centred adducts **16** and **17** assume a conformation at carbon-2 such that the addends occupy pseudo-axial positions. This results in large β-C—H dihedral angles (Table 4). Spin adducts with chiral addends (**7**, **14**, **15**) show no evidence of extra splitting in their EPR spectra, indicating that a fourth chiral centre has no influence on the EPR spectra. The structure of the adducts is such that there are no sufficient interactions between the substituents at the fourth chiral centre to influence the β-hydrogen coupling constants.

In species I of the oxygen-centred spin adducts there are 1,2-diaxial interactions between the addend and the methyne proton in position 3, which are not there in species II. These interactions are such that they lead to a lowering of the β-C—H dihedral angles. As a result of

Table 4. Hyperfine splitting constants of spin adducts of 3,5-diphenyl-5-methylpyrroline-1-oxide (3) in toluene

Radical	Addend	Species	a_N (mT)	$a_{\beta H}$ (mT)	ΔH (mT)	Dihedral angle (°) ($B_{\rho N} = 2.66$ mT)
6	$CH_3(CH_2)_6CH_2$	I	1.430	2.288	0.168	2.196
		II	1.408	1.914	0.093	3.198
7	$CH_3CHCH_2CH_3$	I	1.452	2.332	0.186	2.055
		II	1.386	1.892	0.130	3.250
8	CH_3CHCH_3	I	1.430	2.156	0.186	2.580
		II	1.386	2.024	0.093	2.927
9	C_6H_{11}	I	1.430	2.288	0.168	2.196
		II	1.408	1.892	0.093	3.250
10	CH_3	I	1.408	2.266	0.186	2.264
		II	1.430	1.430	0.130	4.284
11	$CH_2{=}CH$	I	1.452	2.200	0.149	2.457
		II	1.364	1.364	0.149	4.427
12	Ph[a]	I	1.430	2.135	0.093	2.638
		II	1.330	1.602	0.093	3.910
13	$PhCH_2$	I	1.430	2.288	0.186	2.196
		II	1.408	1.672	0.149	3.755
14	$CH_3C(OH)CH_2CH_3$	I	1.496	2.376	0.197	1.907
		II	1.452	1.958	0.125	4.091
15	CH_3CHOH	I	1.451	2.274	0.186	2.239
		II	1.387	1.660	0.168	3.782
16	$(CH_3)_3CO$[b]	I	1.300	1.550	0.093	4.024
		II	1.250	0.725	0.112	5.853
17	HO[c]	I	1.386	1.386	0.075	4.379
		II	1.415	0.950	0.112	5.330
18	H	I	1.375	1.750	>0.010	2.42
				2.213		3.58

[a] $a_{\gamma\text{-H}} = 0.138$ mT.

[b] $a_{\gamma\text{-H}} = 0.15$ mT for I and 0.125 mT for II.

[c] Water used as solvent.

the pseudo-equatorial positions of the addends in the carbon-centred spin adducts, there are no significant differences in the steric interactions between the substituents in both species, but species II has minimum repulsive forces between the addends and the phenyl substituent in position 3 because of their existence on the same side of the molecule.

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